IOP Conf. Series: Materials Science and Engineering **133** (2016) 012032 doi:10.1088/1757-899X/133/1/012032

Special features of structural changes of amorphizing nickel alloys in liquid and heterogeneous state

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Abstract. Polytherms of kinematic viscosity of nickel-based alloys with Cr, Si, Fe and B additives have been studied. It was found out that the first liquid phase volumes appear when temperatures are well below the tabular values of the solidus temperature ts. The critical temperature of the alloy was defined. The ways of obtaining materials of higher amorphization ability were suggested.

1. Introduction

In the process of structure fabrication different types of welding are used. However, technically it is not always appropriate and possible. A very promising alternative to welding is to use solders to connect details made of fundamentally different materials. Soldering has a complex of advantages over welding and its capabilities expand significantly because of the use of solder in metastable state either amorphous or nanocrystalline.

The uniqueness of such solder is provided by the following properties: low melting temperature, homogeneous composition of the whole material volume, increased capillary and adhesion activity, ease of fabricating embedded elements by cutting or by punching.

2. Main part

In the National Research Nuclear University "MEPhI" a complex of works aimed at the development of solders was conducted. This resulted in solving several complex technical tasks [1]. In particular, nickel-based alloys are widely used in aviation technology for soldering of heat exchangers and gas turbine engine blades [2-3], in rocket-and-space technology for soldering rocket engine nozzles, in atomic engineering for soldering stubs, fuel elements [4] and so on. The use of nanocrystalline materials in these fields also greatly simplifies assembly operations and a soldered joint has high reliability at elevated temperatures and non-uniform loads.

The degree of volume amorphization and the structure of nanopowders are essentially determined by the elemental composition. However, an analysis of the reasons for the low quality of products demonstrates the essential role of different methods of obtaining materials by direct synthesis [5-11].

The easiest way to make nanocrystalline powders is to evaporate material at a proper temperature either under inert gas with subsequent condensation of steam or in the reaction zone with the formation of spherical particles, or on surfaces, where particles then will have faceting.

Among all the chemical methods the most widely used one is plasma-chemical method, in which the formation reaction of new phase germs takes place under non-equilibrium conditions at a high speed, but under a low intensity of growth.

Nanoparticle deposition in a colloidal solution involves a process of synthesis, formation of a disperse system and its transition from a liquid state to a dispersed solid one. The method has high selectivity and allows to produce nanopowders with very narrow size distributions.

The most productive method is a mechanical abrasion of components. During this process grinding and a plastic deformation of substances takes place, the mass transfer is accelerated, the mixing of components is performed at an atomic level, and their chemical interaction is activated.

The amorphous or nanocristalline structure of metals and alloys forms at fast (the speed $\geq 10^6$ deg/sec) cooling of the melt on the surface of the spinning disc or drum which is called the process of spinning. When required, an amorphous ribbon is annealed which leads to the formation of the nanostructure.

The melt is analogous to the amorphous material. According to the authors of work [12] the presence of nuclear local nanodomains (clusters) in the structure of amorphous materials and melts is as important for the theory of these condensed states of matter as an elementary cell for the theory of crystals.

Molten materials and alloys are special states of matter, caused by the lack of degenerated interfaces of clusters, a distortion of the translational symmetry, more electronic density in clusters as compared to the inter-cluster space, and an increased dynamic excitation of atoms in an outer atomic layer of clusters. The part of the last-mentioned ones in total volume of the matter is greater than 15%.

The role of the outer atomic layers of clusters for the formation of the structure and properties of materials becomes even more significant, given their different electronic configurations due to the change of valence and a decrease of electron density. The result of these changes is weakening of the interatomic interaction with other atoms of the cluster and a higher amplitude of oscillations.

The multiformity of a short-range order structure of burden materials determines a non-equilibrium and heterogeneity of the structure, achieved in the melting process of melts. However, the non-equilibrium is stipulated by an uneven distribution of atoms in liquid metal within the nanovolume space, and the heterogeneity is stipulated by an uneven distribution of clusters differing in structure within the nanovolume of the matter.

The speed at which the equilibrium is reached in metallic melts is much slower than changes of external environments. This determines the prolonged retention of the non-equilibrium states. As a result, the melts of the identical composition can be distinguished by short-range order parameters, the nature of inter-particle interactions and the distribution of elements and, therefore, the conditions of diffusion processes, crystallization, and others [5].

Numerous experimental data testify to the existence of the following patterns: the higher is the melt equilibrium and the homogeneity before the solidification, the better are the quality parameters of the solid metal [5-7].

The equilibrium can be achieved in different ways, but long-term experience shows that the maximum efficiency can be achieved by the temperature-time processing (TTP) of the melt during the melting process [5-11]. TTP processing modes are set by analyzing the results of the research of physical and chemical properties of the melt, as well as the micro-structure and properties of the solid metal.

Investigation of properties of melts, in particular, of kinematic viscosity (ν) is of a great interest to understand the processes occurring in the heterogeneous field, i.e. in the solidus-liquidus temperature range. Soldering technology provides for the formation of a liquid phase with further transition of the forming joint into the liquid-solid and solid-liquid, and then into the solid state. Because of the inability to accurately determine the relation of these phases due to the lack of many-component state diagrams, the methods to study the melt properties are used. In particular, the results of the study of viscosity for the first time allowed authors to determine the interface between the solid-liquid and liquid-solid states of iron-carbon alloys.

Thus, the study of the concentration and temperature dependences of melt properties allows to scientifically justify optimum modes of melting and to study the effect of liquid metal on the processes of the structure formation in the heterogeneous field.

Studies on temperature dependences of kinematic viscosity ν of nickel-based solder samples STEMET 1301, with additives of Cr, Si, B and Fe are given in figure 1. According to the developers the solidus temperature of the studied compound is 980°C and the liquidus temperature is 1010°C. The alloy is suitable for soldering of stainless steels, dispersion-strengthened steels, nickel-based heat-resistant melts and nichrome at temperatures of 1010-1170°C.

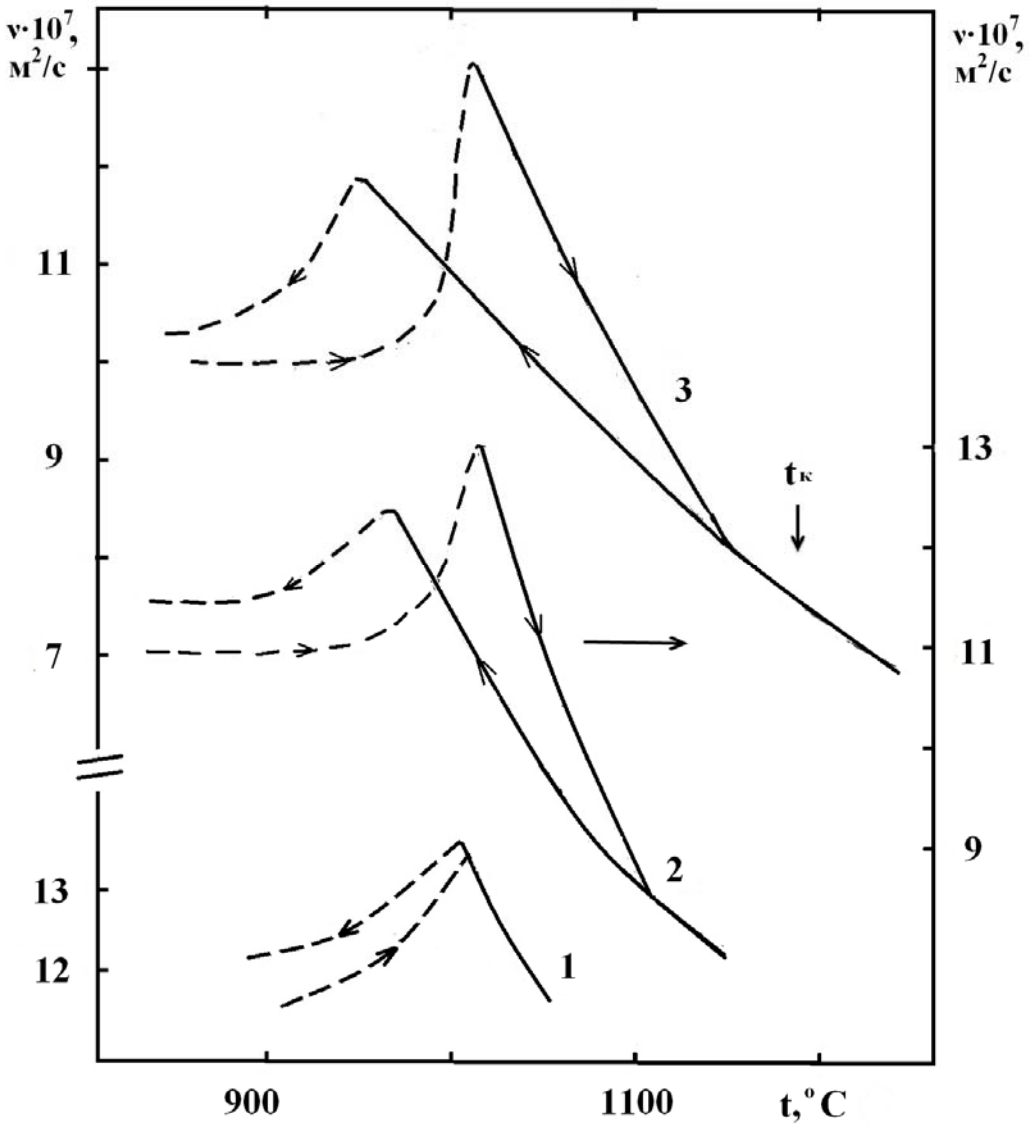

Figure 1. Temperature dependences of the kinematic viscosity (ν) of STEMET 1301 alloy during heating and cooling.

Amorphization of materials is carried out when relationship between amorphization temperature (t_a) and liquidus temperature (t_L) is t_a/ t_L=0.45. The required temperature for a given alloy t_a=440°C is assured by the sharp supercooling of the melt at a high cooling rate, the presence of silicon and boron in the alloy composition, which together with the basic elements forms complex low-melting eutectic molecular entities, and by other factors. The process is accompanied by an increase in viscosity by 10-15 times.

Viscosity polytherms which are represented on figure 1 consist of two parts. The left picture shows the temperature dependence on the attenuation decrement (δ) of combined oscillations of the crucible

with the melt which is suspended on an elastic metal thread (broken line). This sensor is for the determination of the absolute values of kinematic viscosity by the method of Shvidkovskiy E.G. A conversion of the value δ into values ν will not allow to show dependency ν (t) in the studied temperature range, since "melt-solid" state in heterogeneous field exceeds the viscosity value of molten metal in tens of times.

The processes occurring in a heterogeneous field are important for solders, since the formation of the joint structure and of its properties takes place below the liquidus temperature.

When the solder is heated, the first volumes of liquid metal appear long before the solidus temperature is reached and the attenuation decrement is slowly increasing. Reaching of solidus temperature known from the work [12], is accompanied by a dramatic increase in value δ, i.e. the amount of the molten metal increases.

Further heating above t_L is accompanied by the reduction of the ν melt in accordance with the well-known exponent ν(t). When cooled at the temperature higher than 1150^{o}C the polytherm does not coincide with the dependency obtained by heating. There is branching or a hysteresis of polytherms. In the heterogeneous field the value of δ is higher when cooled than when heated.

When cooled at the temperature higher than 1230^o C the hysteresis value is increasing and the critical temperature is close to 1180^{o}C.

3. Conclusions

Thus, the study of the liquid alloy STEMET 1301 led to the following conclusions:

- the first liquid phase volumes appear when temperatures are well below the tabular values of solidus temperature t_s;
- the intensive growth of the liquid phase volume in heterogeneous field is observed, when the temperature is close to t_s, and it ends at $t_{L;}$
-when the temperature increases further, the viscosity polytherms have a classic exponential type, typical of metallic liquids;
- polytherms ν in the heating-cooling mode coincide only when the super-heating temperature is not a 100^{o}C higher, than t_L. A further increase in heating temperature leads to the hysteresis of polytherms, where its value remains constant only when the heating temperature of the melt reaches its critical point. When the melt is cooled polytherms ν are located below ν (t) when heated. In the heterophase field the viscosity value or the attenuation decrement of oscillations is higher than when cooled;
- the higher is the heating temperature of the melt in relation to $t_{(L)}$, the greater is the degree of supercooling during the solidification process;
- setting of exposure time of the melt at a temperature of 1150^{o}C for 75 minutes allows to reduce the critical temperature by 100^{o}C;
-considerable supercooling of the melt after the high-temperature heating and elevated values of attenuation decrement in the heterogeneous field contribute to obtaining of the highly amorphized material in the process of rapid hardening. This material is characterized by less surface roughness of the film, better ductility properties and good manufacturability in the process of fabricating of embedded elements;
- the nanocrystalline material obtained by the crystallization of the amorphous films, is qualitatively different from other nanopowders, obtained under other technologies by the distribution of elements and dimensional uniformity.

Acknowledgments

This work was supported by the Scientific researches of higher education institutions within the State task of the Russian Federation No. 2014/236.

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